

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-131516

(43)Date of publication of application : 15.05.2001

(51)Int.Cl.

C09J163/00

(21)Application number : 11-319041

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(22)Date of filing : 10.11.1999

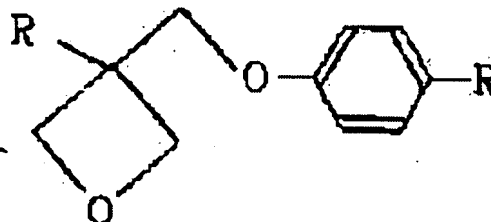
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(54) CATIONIC CURABLE ADHESIVE COMPOSITION EXHIBITING HIGH ADHESIVITY TO HARD ADHESIVE MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a cation curable adhesive composition which exhibits high adhesivity to hard adhesive plastics represented by polyolefins and to various hard adhesive materials.

SOLUTION: This cation curable adhesive composition comprising a phenoxymethyloxetane of the general formula (R is a 1 to 5C alkyl group), an epoxy compound having an epoxy group or an alicyclic epoxy group and a cation curing catalyst as main components, wherein the phenoxymethyloxetane and the epoxy compound are compounded in a weight ratio of the phenoxymethyloxetane to the epoxy compound of 40:60 to 95:5.



LEGAL STATUS

[Date of request for examination]

08.11.2006

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

2, 13, 3
ep-pbd

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the cation hardening mold adhesives constituent which presents a high adhesive property to various difficulty adhesive property ingredients, such as plastics represented by polyolefines.

[0002]

[Description of the Prior Art] The plastic material represented by polyolefines is known as a difficulty adhesive property ingredient. As adhesives used for this kind of difficulty adhesive property ingredient, hot melt system adhesives, the cyanoacrylate adhesive which used the primer together, the radical hardening mold acrylic adhesives which need the surface preparation of adherend, an acrylic binder, etc. are known conventionally.

[0003]

[Problem(s) to be Solved by the Invention] However, these well-known adhesives have the following fault, respectively.

[0004] Since use is presented with hot melt system adhesives hot melt system adhesives in the state of heating, use is restricted by the thermal resistance of the ingredient which should be pasted up.

[0005] Cyanoacrylate adhesive cyanoacrylate adhesive does not present sufficient result to various environmental tests-proof, but is lacking in dependability.

[0006] Acrylic adhesives acrylic adhesives do not present sufficient result like **** to various environmental tests-proof hardening is not only checked by oxygen, but, but are lacking in dependability.

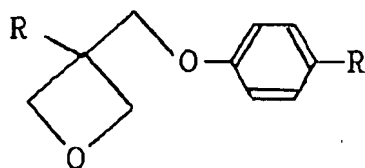
[0007] An acrylic binder acrylic binder has low bond strength, and for this reason, there is also an example currently used in the lamination of films, but in the field as which structural reinforcement is required, it is unsuitable.

[0008] Epoxy system-cationic polymerization mold adhesives are also known besides the above-mentioned various adhesives. It excels also in solvent resistance, without hardening inhibition of this being carried out by oxygen, and the adhesive property over the difficulty adhesion plastic material represented by polyolefines although it has the outstanding properties, such as low out gas and low hardening shrinkage characteristics, is very low.

[0009] Then, it is in the purpose of this invention offering the cation hardening mold adhesives constituent which improved the fault which presents a high adhesive property to various difficulty adhesive property ingredients, such as difficulty adhesive property plastic material represented by polyolefine, and consists in an above-mentioned well-known technique.

[0010]

[Means for Solving the Problem] According to [in order to attain the above-mentioned purpose] this invention, it is a general formula [** 2].



(R contains the phenoxymethyl oxetane which has alkyl group) of carbon numbers 1-5, the epoxy compound which has an epoxy group or an alicycle epoxy group, and a cation curing catalyst as a principal component, and it is characterized by said phenoxymethyl oxetane and the rate of a compounding ratio of an epoxy compound being phenoxymethyl oxetane:epoxy compound =40:60-95:5 in a weight ratio.

[0011]

[The mode of implementation of invention] Hereafter, this invention is explained in full detail concretely.

[0012] Although the phenoxymethyl oxetane which has the above-mentioned general formula used for this invention is specifically 3-methyl (or ethyl, propyl, butyl, pentyl) [(phenoxy) methyl (or ethyl, propyl, butyl, pentyl)] -3 oxetane etc., as a desirable example, 3-ethyl-3-[(phenoxy) methyl] oxetane is especially mentioned in this.

[0013] Moreover, the epoxy compound used for this invention is an epoxy compound which has an epoxy group or an alicycle epoxy group. As a compound which has an epoxy group, it is specifically a polybutadiene system epoxy compound (as an example). Trade name: The product made from PB3600 Die Cel Chemistry, the bisphenol A mold epoxy compound (as an example) Trade name: The product made from 850S Dainippon Ink Manufacture, a phenol novolak mold epoxy compound (as an example) Trade name: N740 As a compound which the product made from Dainippon Ink Manufacture etc. is mentioned, and has an alicycle epoxy group, trade names ERL4206 (made in Union Carbide) and ERL4221 (made in Union Carbide) etc. are mentioned. In this invention, although it is desirable to use it combining the compound which has an epoxy group, and the compound which has an alicycle epoxy group as for these, it can also be used independently, respectively.

[0014] The rate of a compounding ratio of the above-mentioned phenoxymethyl oxetane and an epoxy compound in this invention is a weight ratio, the range of it is phenoxymethyl oxetane:epoxy compound =40:60-95:5, and if it deviates from this range, it cannot present a high adhesive property to a difficulty adhesive property ingredient, and cannot do this invention effectiveness so.

[0015] Furthermore, the cation curing catalysts used for this invention are an optical cation curing catalyst and a heat cation curing catalyst. As an optical cation curing catalyst, an antimony system sulfonium salt compound (for example, trade name SP170 Asahi Denka Kogyo K.K. make) and the Lynn system sulfonium salt compound (for example, trade name SP150 Asahi Denka Kogyo K.K. make) are mentioned, and an antimony system sulfonium salt compound (for example, trade name SI-100L 3 Japanese Federation of Chemical Industry Workers' Unions make) is specifically mentioned as a heat cation curing catalyst.

[0016] The cation hardening mold adhesion constituent concerning above-mentioned this invention is made to intervene between the of-the-same-kind ingredients of the difficulty adhesive property plastic material represented by polyolefines, or the dissimilar materials of this and borosilicate glass, and, in the case of [2] an optical cation curing catalyst (for example, dose 3000 mJ/cm), is. Ultraviolet rays are irradiated, and are hardened, it heats and hardens in the case of a heat cation curing catalyst, for example, oven with a temperature of 120 degrees C, and a high adhesive property is presented.

[0017] As above-mentioned difficulty adhesive property plastic material, ZEONEX (it is a cyclopentadiene system polymer and used as an optical lens and a disk ingredient) by Nippon Zeon Co., Ltd., polypropylene (PP), a liquid crystal polymer (LCP), an acrylonitrile-butadiene-styrene polymer (ABS), polybutylene terephthalate (PBT), a polypropylene ROPIRESARU fight (PPS), polystyrene (PS), polyimide (PI), etc. are mentioned.

[0018]

[Example] Hereafter, as for this invention, the right range is not restricted by these examples although this invention is concretely explained in full detail according to an example.

[0019] [Example 1] Sample No.1-11 were prepared at the rate of a compounding ratio shown in Table 1 using each component of following (1) - (4).

(1) 3-ethyl -3 [(phenoxy) methyl] oxetane : trade name PhOX Toagosei make.

(2) Polybutadiene system epoxy compound : trade name PB3600 Product made from Die Cel Chemistry.

(3) Alicycle epoxy compound : trade name ERL4206 Made in Union Carbide.

(4) Antimony system sulfonium salt compound (optical cation curing catalyst: trade name SP-170 Asahi Denka Kogyo K.K. make.)

[0020] The adhesive strength test was performed about each [these] sample, using trade name ZEONEX by Nippon Zeon Co., Ltd. as difficulty adhesive property plastic material. The trial was performed as follows. First, ZEONEX was cut out in 2.5cm long, 1.5cm wide, and magnitude with a width of face of 5.0mm, and the test piece was produced. Subsequently, exposure 3000 mJ/cm² after applying each sample to this test piece in the thickness of 50 micrometers, and an adhesion area phi of 6mm, inserting with a test piece of the same kind and sticking Ultraviolet rays were irradiated and were stiffened.

[0021] About each pasted-up test piece, the cleavage test was performed using the autograph (Shimadzu make), the adhesive property over ZEONEX was measured, and the result was shown in Table 1.

[0022]

[Table 1]

(単位:重量部)

成分	試料No	1	2	3	4	5	6	7	8	9	10	11
PhOX		30	40	50	60	70	80	90	90	90	95	100
PB3600		50	50	40	30	20	10	5	10	—	3	—
ERL4206		20	10	10	10	10	10	5	—	10	2	—
SP-170		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
試験結果												
接着強度 (kg)		0.15kg /6mmφ	0.89kg /6mmφ	0.91kg /6mmφ	0.96kg /6mmφ	1.15kg /6mmφ	5.15kg /6mmφ	5.31kg /6mmφ	5.65kg /6mmφ	5.39kg /6mmφ	6.02kg /6mmφ	測定 不能

[0023] Table 1 shows the following thing. As shown in sample No.2-10, the rate of a compounding ratio of phoxymethyl OKISEDAN and an epoxy compound is all presenting high cleavage strength within the limits of 40:60-95:5 by the weight ratio. moreover, sample No. which contains either PB3600 or ERL4206 as an epoxy compound -- the cleavage test result also with good 8 and 9 is shown.

[0024] However, it reached sample No.1 and the rate of a compounding ratio of phoxymethyl OKISEDAN and an epoxy compound has deviated from the above-mentioned range in 11. Among these, in sample No.1, bond strength is 0.15kg/16mmphi, and is greatly inferior to sample No.2-10.

Moreover, sample No.11 The coat which can evaluate bond strength then was gelation rather than it was not formed but called it hardening.

[0025] [Example 2] The adhesive trial by the dissimilar materials of various difficulty adhesion plastic material and borosilicate glass was performed about sample No.6 of Table 1. As various difficulty adhesive property plastic material, polypropylene (PP), a liquid crystal polymer (LCP), an acrylonitrile-butadiene-styrene polymer (ABS), polybutylene terephthalate (PBT), polypropylene sulfide (PPS), polystyrene (PS), and polyimide (PI) were used.

[0026] They are ultraviolet rays after use adhesion plastic material various [above-mentioned] as 2.5cm long, 1.5cm wide, and a test piece with a width of face of 3.0mm, and using borosilicate glass as 2.5cm long, 1.0mm wide, and a test piece with a width of face of 1.0mm, applying sample No.6 to one side of these test pieces in the thickness of 50 micrometers, and an area phi of 6mm, putting the test piece of another side on this and sticking Exposure 3000 mJ/cm² It was made to irradiate and harden. The cleavage test was performed like the example 1 using the autograph (Shimadzu make) about the obtained test piece, and the result was shown in Table 2.

[0027]

[Table 2]

試 験 片	P P / ガラス	L C P / ガラス	A B S / ガラス	P B T / ガラス
接着強度	5. 0 2 kg / 6 mmφ	6. 0 9 kg / 6 mmφ	7. 4 4 kg / 6 mmφ	7. 6 3 kg / 6 mmφ
(破壊モード)	P P から界面破壊	ガラス材破	ガラス材破	ガラス材破

試 験 片	P P S / ガラス	P S / ガラス	P I / ガラス
接着強度	5. 8 0 kg / 6 mmφ	4. 4 6 kg / 6 mmφ	8. 8 0 kg / 6 mmφ
(破壊モード)	P P S から界面破壊	P S から界面破壊	ガラス材破

[0028] Table 2 shows that this invention sample presents a high adhesive property also between a difficulty adhesive property ingredient and a different ingredient from this.

[0029] [an example 3] -- the ** which does not change the amount of catalysts instead of curing catalyst SP-170 about sample No.6 of Table 1 -- a following catalyst (A) and (B), i.e., a (A) light cation curing catalyst:Lynn system sulfonium salt compound, (SP150 Asahi Denka Kogyo K.K. make)

(B) Heat cation curing catalyst : antimony system sulfonium salt compound (SI-100L 3 Japanese Federation of Chemical Industry Workers' Unions make)

It considered as the ***** samples A and B, and the adhesion test was performed like the example 1.

[0030] The adhesion test was performed as follows. First, ZEONEX is used as 2.5cm long, 1.5cm wide, and a test piece with a width of face of 5.0mm, Samples A and B are applied to this in the thickness of 50 micrometers, and an area phi of 6mm, respectively, lamination and ultraviolet rays (exposure 3000 mJ/cm²) were irradiated, and the test piece of ZEONEX was stiffened. Subsequently, the cleavage test was performed for the obtained test piece using the autograph (Shimadzu make) like the example 1, and the result was shown in Table 3.

[0031]

[Table 3]

試 験 \ 試 料	A	B
接 着 強 度	5.72 kg / 6 mm ϕ	5.81 kg / 6 mm ϕ

[0032] Table 3 shows that each presents a high adhesive property, even if a curing catalyst is an optical cation curing catalyst and it is a heat cation curing catalyst.

[0033] [Example 4] Sample No.12 -15 were prepared at the rate of a compounding ratio shown in Table 4 using each component of following (1) - (7).

(1) PhOX It is the same as an example 1.

(2) PB3600 ** (3) ERL4206 ** (4) bisphenol A mold epoxy oligomer : trade name 850S Product made from Dainippon Ink Manufacture.

(5) Phenol novolak mold epoxy oligomer : trade name N740 Product made from Dainippon Ink Manufacture.

(6) Alicycle epoxy compound : trade name ERL4221 Made in Union Carbide.

(7) SP170 It is the same as an example 1.

[0034] The cleavage test was performed like [sample / each / these] the example 1, the adhesive property over ZEONEX was measured, and the result was shown in Table 4.

[0035]

[Table 4]

(重量部)

成分 \ 試料No.	12	13	14	15
P h O X	9 0	9 0	9 0	9 0
P B 3 6 0 0	—	—	—	—
E R L 4 2 0 6	1 0	1 0	—	—
8 5 0 S	1 0	—	1 0	—
N 7 4 0	—	1 0	—	1 0
E R L 4 2 2 1	—	—	1 0	1 0
S P - 1 7 0	2. 0	2. 0	2. 0	2. 0
試 験 結 果				
接着強度 (kg)	6.33kg /6mm ϕ	6.07kg /6mm ϕ	5.65kg /6mm ϕ	3.83kg /6mm ϕ

[0036] Table 4 shows presenting the bond strength which was excellent in all of sample No.12 -15, and presenting a high adhesive property to difficulty adhesive property plastic material.

[0037]

[Effect of the Invention] A high adhesive property is presented to various difficulty adhesive property ingredients, such as difficulty adhesive property plastic material represented with the former by the polyolefine which was not able to be pasted up in phenoxymethyl oxetane since this invention was made to contain as a principal component as above in addition to an epoxy compound.

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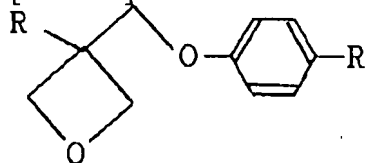
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CLAIMS

[Claim(s)]

[Claim 1] General formula [** 1]



(R is a cation hardening mold adhesives constituent which presents a high adhesive property to the difficulty adhesive property ingredient which contains the phenoxymethyl oxetane which has alkyl group) of carbon numbers 1-5, the epoxy compound which has an epoxy group or an alicycle epoxy group, and a cation curing catalyst as a principal component, and is characterized by said phenoxymethyl oxetane and the rate of a compounding ratio of an epoxy compound being phenoxymethyl oxetane:epoxy compound = 40:60-95:5 in a weight ratio.

[Claim 2] The cation hardening mold adhesives constituent which presents a high adhesive property in claim 1 to the difficulty adhesive property ingredient according to claim 1 said whose phenoxymethyl oxetane is 3-ethyl -3 [(phenoxy) methyl] oxetane.

[Claim 3] The cation hardening mold adhesives constituent which presents a high adhesive property in claim 1 to the difficulty adhesive property ingredient according to claim 1 which are a kind or two or more sorts of combination as which said epoxy compound was chosen from the group of a polybutadiene system epoxy compound, the bisphenol A mold epoxy compound, a phenol novolak mold epoxy compound, and an alicycle epoxy compound.

[Claim 4] The cation hardening mold adhesives constituent which presents a high adhesive property in claim 1 to the difficulty adhesive property ingredient according to claim 1 said whose cation curing catalyst is an optical cation curing catalyst or a heat cation curing catalyst.

[Translation done.]